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Investigation of the Effects on Covalency and Ionicity on 4*f*-5*d* Transition Energy of Ce^{3+} in Oxides and Fluorides

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$Y_3Al_5O_{12}$ crystal including Ce^{3+} substituted for Y^{3+} (YAG: Ce^{3+}) is widely used for yellow phosphor in white LED because its crystal structure is stable and it shows emission spectra with broad band. The other garnet-type oxides and some fluorides are also considered as host crystals for phosphors to improve luminescent efficiency and other physical properties. The 4*f*-5*d* transition of Ce^{3+} in various crystals have been actively investigated experimentally and theoretically. Based on the systematic analysis of the experimental data, Dorenbos proposed an empirical equation to predict the spectroscopic redshift D(A) based on the centroid shift and the crystal field splitting. The systematic first-principles calculations of the electronic structure of Ce^{3+} in various crystals were performed by Higashiura [1]. He found that the centroid shift of the 4*f*-5*d* transition energy of Ce^{3+} is mainly determined by the charge transfer from O^{2-} to Ce^{3+} and showed that the charge transfer has a good correlation with the centroid shift of the 4*f*-5*d* transition energy of Ce^{3+}. In this work, the systematic first-principles calculations of the electronic structure of Ce^{3+} in various crystals were performed in an improved computational condition and the results were analyzed in more detail. The 4*f*-5*d* transition spectra of Ce^{3+} in various oxides were also calculated from first-principles and compared.

The CeO_8 cluster models were constructed based on the crystal structures of the host crystals. The effective Madelung potential was produced by locating several thousand point charges at the atomic sites outside the cluster. The molecular orbital calculations were performed based on the relativistic discrete variational-Xα (DV-Xα) method. The relativistic Vosko-Wilk-Nusair (RVWN) potential was used as the exchange correlation potential. The effect of the lattice relaxation was considered by changing the Ce-O bond lengths based on the difference in the Shannon's crystal radii.

The correlation diagram between the theoretical 4*f*-5*d* transition energy and the experimental 4*f*-5*d* transition energy was constructed. Although the experimental values of YIG:Ce^{3+} and HoAG:Ce^{3+} have not been reported, the experimental values for them were predicted from the theoretical values based on the diagram. The correlation diagram between the net charge of Ce and the calculated centroid shift was also constructed based on the first-principles calculation. Although there are some exceptions, the centroid shift has a good correlation with the net charge of Ce. The theoretical absorption spectra of Ce^{3+} in $Gd_3Al_5O_{12}$ (GAG), $Ho_3Al_5O_{12}$ (HoAG), $Lu_3Al_5O_{12}$ (LuAG), $Tb_3Al_5O_{12}$ (TAG), $Y_3Al_2Ga_3O_{12}$ (YA2G3G), $Y_3Al_3Ga_2O_{12}$ (YA3G2G), $Y_3Al_4GaO_{12}$ (YA4GG), $Y_3Al_5O_{12}$ (YAG), $Y_3AlGa_4O_{12}$ (YAG4G), $Yb_3Al_5O_{12}$ (YbAG), $Y_3Ga_5O_{12}$ (YGG), and $Y_3Fe_5O_{12}$ (YIG) were calculated from first-principles and compared. The theoretical absorption spectrum for Ce^{3+} in YAG was in good agreement with the experimental one and the host dependence of the absorption spectra was predicted theoretically.

[Reference]

[1] K. Higashiura, *Master thesis*, Kwansei Gakuin University (2012).